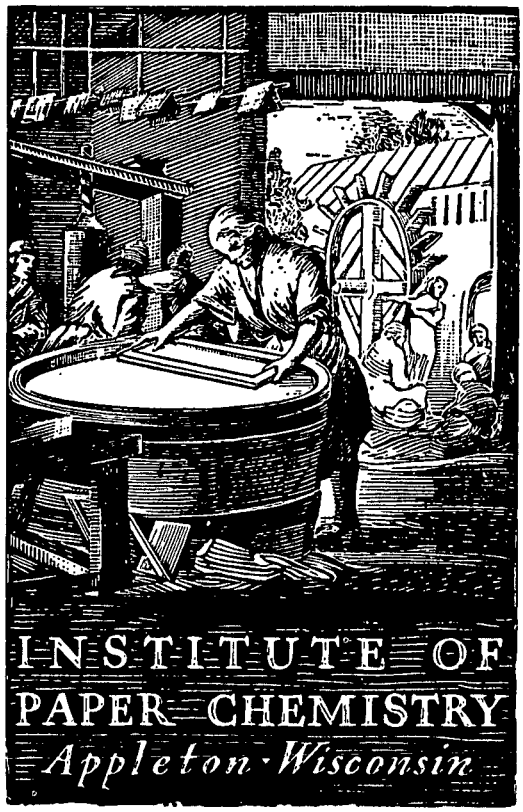

EFFECT OF OXIDATIVE PULPING CONDITIONS ON THE TALL OIL AND TURPENTINE COMPONENTS OF SOUTHERN PINEWOOD

Project 3266

Report Two
Final Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 9, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

EFFECT OF OXIDATIVE PULPING CONDITIONS ON THE TALL OIL AND TURPENTINE COMPONENTS OF SOUTHERN PINEWOOD

Project 3266

Report Two

Final Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 9, 1976

TABLE OF CONTENTS

LIST OF TABLES

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

EFFECT OF OXIDATIVE PULPING CONDITIONS ON THE TALL OIL AND TURPENTINE COMPONENTS OF SOUTHERN PINEWOOD

SUMMARY

Oxygen/alkali studies were conducted with aspen chips, fiberized red maple, loblolly pine chips and fiberized wood, and normal and lightered slash pine chips. Refined tall oil acids and sulfate turpentine were cooked in the absence of wood and in the presence of chips and fiberized wood. Although pulp yields were somewhat lower in oxygen/sodium hydroxide than in oxygen/sodium carbonate and bicarbonate systems, the yields of tall oil and turpentine were somewhat lower in the carbonate systems. These findings were interpreted as the results of a possible difference in the chemical mechanisms between oxygen/hydroxide and oxygen/carbonate systems.

In oxygen/sodium hydroxide, wood appeared to be attacked preferentially over the tall oil. With turpentine the amount and physical form of the wood were of minor importance in its survival.

The lowest yields, 15-25%, of tall oil were obtained in oxygen/sodium hydroxide in the absence of wood. The presence of wood improved the recovery to 60-80%. In oxygen/carbonates, the survival of tall oil was less "protected" by wood than in the oxygen/hydroxide system with yields of 45-50%.

The main changes in the acids were a relatively faster rate of disappearance of linoleic acid than oleic acid, and the disappearance of abietic acid by conversion to dehydroabietic acid, especially in oxygen/carbonates.

Turpentine survival was greater in oxygen/sodium hydroxide (19-38%) than in the carbonate systems (9-18%). The "protective" action of wood, as seen with tall oil, was nearly absent in turpentine survival.

Based on the results of these studies, the recovery of tall oil and turpentine may be practical only in preoxygen stages of oxygen/alkali pulping.

OBJECTIVES

The objectives are: (1) To determine the effects of oxygen/alkali pulping conditions on the tall oil and turpentine precursors (extractives) of southern pinewood, (2) to characterize the products of reactions of these extractives under a variety of such pulping conditions, (3) to determine, if possible, the conditions under which tall oil and turpentine components can be salvaged, and (4) to consider the possible recovery of tall oil and turpentine components from preoxygen stages of multistage oxygen/alkali pulping processes.

REVIEW OF OBJECTIVES AND PROGRESS TOWARD THEIR ATTAINMENT

OBJECTIVE 1

Work on the project "to determine the effects of oxygen/alkali pulping conditions on tall oil and turpentine precursors" was directed toward the recovery of extractable crude tall oil and steam-distillable turpentine. Conditions were varied to include atypical and exaggerated factors in order to expose or emphasize some of the possible losses due to oxidation and chemical degradation. The main wood components appeared to react faster than the extractives and, therefore, appeared to "protect" the tall oil precursors from attack.

OBJECTIVE 2

No effort was made to recover and identify the products formed from the extractives. To do so would have required a long range study with pure compounds, requirements which were beyond the provisions of Project 3266. Work along these lines is in progress (1976) in a doctoral thesis (IPC) by Gerald R. Mittet, "Degradation of fatty acids, fats, and waxes by molecular oxygen in alkaline media."

The most obvious chemical effects were (1) general oxidation of tall oil acids and turpentine, (2) more rapid loss of linoleic acid than of oleic acid, and (3) conversion of abietic acid to dehydroabietic acid.

OBJECTIVES 3 AND 4

The most obvious route for the recovery of the maximum yields of tall oil may be to process an alkaline impregnation liquor from a preoxygen step. However, one-stage high-yield oxygen/alkali pulping may produce black liquors

which can be processed in ways similar to kraft black liquors for tall oil soap skimming. The possible protective action by the wood against the oxidative destruction of tall oil and turpentine precursors may obviate the necessity of a two-stage process in order to recover these by-products.

Based on the work of Project 3266 and on published accounts of oxygen/alkali pulping, one of the critical factors is that of oxygen-transfer across the gas-liquid interface to maintain useful levels of dissolved oxygen in the cooking liquor. Some light may be shed on this phenomenon through the work currently in progress on Project 3265, "Carbohydrate peeling and stopping reactions in oxygen/alkali pulping."

INTRODUCTION

The initial effort to determine the extent to which tall oil survives oxygen/alkali pulping was reported in Project 3266, Report One (1). Although the data indicated that considerable losses occurred in the pulping experiments, the conclusions were tentative and subject to modification as additional data became available. Thus, the considerable losses of tall oil were due mainly to incomplete recovery in the analyses. When all liquors as well as residual pulps were analyzed, the recovery of tall oil was substantial and compared favorably with tall oil recovery in the kraft process (2). No attempt was made to study degradation products of tall oil components.

The second phase of the work on Project 3266 is reported herewith, and includes a section on turpentine. As in the work with tall oil, no attempt was made to recover and identify products of oxidized and degraded turpentine components.

RESULTS AND DISCUSSION

OXYGEN/SODIUM HYDROXIDE PULPING OF ASPEN AND NORMAL AND RESIN-SOAKED (LIGHTERED) SLASH PINE

One approach to the study of the fate of tall oil precursors in oxygen/alkali pulping was that of cooking both softwoods and hardwoods. Further, the cooking of a highly resinous wood, such as lightered wood, was included in the hope of magnifying possible changes in the composition of extracted crude tall oil (CTO). Thus, a series of four oxygen/sodium hydroxide cooks was obtained with aspen, and normal and Paraquat-treated (3) slash pine (1). The results of tall oil recovery and pulp yield were reported previously and are repeated, for ease of reference, in Table I. In addition, Tables I and II list the results of the fractionation of the crude tall oils and analysis by gas chromatography, respectively.

It seems noteworthy that the yield of crude tall oil was somewhat greater than would have been predicted, based on the apparent crude tall oil obtained by saponifying the extractives. This was found both for aspen and normal slash pine. The results for the Paraquat-treated slash pine may reflect, in part, the presence of large amounts of turpentine usually found in such trees. Obviously, most of the turpentine would escape recovery in the procedure used to extract the crude tall oil (see section on Turpentine, p. 29).

The fractionation of the crude tall oil on DEAE-Sephadex (4) and by differential methylation produced data shown in Tables I and II, for wood extractives and for tall oils formed in the corresponding oxygen/sodium hydroxide cooks. The results showed that the neutrals (unsaponifiables) were proportionately larger in the aspen than in the slash pine extracts.

TABLE I

FRACTIONATION OF SAPONIFIED EXTRACTIVES (ACETONE), AND OF EXTRACTED CRUDE TALL OIL (CTO) FROM OXYGEN/SODIUM HYDROXIDE PULPING OF CHIPS OF ASPEN, NORMAL SLASH PINE, AND PARAQUAT-TREATED SLASH PINE[a]

	Aspen			Normal Slash Pine, control			Paraquat-treated Slash Pine						
							Nonresin-soaked Wood			Resin-soaked Wood			
Extractives (acetone), % o.d. wood	3.3			3.9			8.2			34			
Apparent CTO after saponification of extractives, % o.d. wood	1.04			1.67			6.7			33			
Yield of pulp, % o.d. wood[b]	73			59			71			69			
Total CTO from O_2/alkaline pulp, % o.d. wood	1.30			1.93			2.58			19.8			
	Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Extract of Wood Un-sapfd.	Extract of Wood Sapfd.	Decanted Liquor	Extract of Acid. Pulp
CTO, % of total CTO	--	8.3	20.8	--	16.1	22.7	--	26.9	20.8	--	--	72	4.0
Fractionation of CTO[b], % of CTO													
Neutrals	43.3	31.4	58.3	10.4	22.9	12.6	6.6	16.1	16.7	9.7	8.4	10.1	16.1
Fatty acids	53.1	49.3	37.9	68.4	52.6	68.8	32.2	51.1	45.5	6.4	8.3	9.9	8.5
Resin acids	3.0	18.8	0.87	16.1	19.4	13.1	46.5	32.1	30.4	59.0	67.1	48.6	56.4
Total recovered	99.4	99.5	97.1	94.9	94.9	94.5	85.3	99.3	92.6	76.1	83.8	68.6	81.0

[a] In each cook 45 g of o.d. wood was pulped at 22% sodium hydroxide, liquor/wood ratio 3.85, under 140 psig of oxygen gas at 160°C for 2 hr.

[b] These data appeared in Progress Report One, Table IV, p. 12.

TABLE II

ANALYSIS BY GAS CHROMATOGRAPHY (GC) OF THE ACID FRACTIONS FROM THE OXYGEN/SODIUM HYDROXIDE COOKS LISTED IN TABLE I

Analysis of Acid Fractions[a] by GC, % of fraction anal.	Retention Time, min	Aspen			Normal Slash Pine, control			Paraquat-treated Slash Pine						
								Nonresin-soaked Wood			Resin-soaked Wood			
											Extract of Wood			
		Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Extract of Wood, sapfd.	Decanted Liquor	Extract of Acid. Pulp	Unsapfd.	Sapfd.	Decanted Liquor	Extract of Acid. Pulp
Fatty acids, % CTO[b]			31.4	36.3	67.8	52.9	68.1	31.4	43.0	44.4	3.7	7.1	8.1	6.8
<C_{16}		5.9	9.4	3.9	1.6	2.0	1.6	1.4	<1	1.3	3.5	6.2	3.5	2.7
Palmitic	4.5	17.5	13.6	10.6	6.7	9.2	5.6	7.0	7.4	7.0	11.7	8.3	8.0	10.2
Palmitoleic	5.5	<1	1.2	1.9	1.3	2.0	1.4	1.8	2.0	2.3	3.9	3.1	3.2	3.0
C_{17} + Unknown	6.7;7.2	1.7	<1	<1	<1	<1	<1	<1	<1	<1	<1	1.6	<1	<1
Stearic	8.1	4.0	3.1	2.9	1.3	2.3	1.2	1.5	1.6	1.6	3.7	3.1	2.7	3.0
Oleic	9.6	7.9	9.1	10.2	38.9	40.2	35.7	40.4	44.5	36.0	43.4	33.8	35.3	39.2
C_{19}	11.0	<1	<1	<1	<1	<1	<1	1.0	<1	<1	<1	1.0	1.0	1.0
Linoleic	12.3	52.7	57.4	60.8	38.4	33.8	40.5	36.8	35.1	37.9	27.4	30.3	30.9	32.4
Arachidic (C_{20})	13.9	2.5	1.2	1.9	3.1	2.7	3.6	3.1	1.6	3.4	3.4	3.1	3.6	2.2
Linolenic	16.6	3.7	2.4	4.8	2.2	2.1	2.7	1.5	1.6	2.8	<1	3.0	2.7	1.7
Unknown	21.8	<1	<1	<1	<1	1.0	1.1	<1	<1	1.3	<1	1.6	2.0	<1
Behenic (C_{22})	24.5	2.5	1.8	2.4	4.9	4.0	5.7	4.6	4.3	5.9	3.0	4.8	5.8	3.3
Oleic/linoleic ratio		0.15	0.16	0.17	1.01	1.19	0.88	1.10	1.27	0.95	1.58	1.12	1.14	1.21
Resin acids,[c] % CTO[b]		0.66	4.5	0.87	16.1	9.4	12.5	44.7	28.7	30.0	59.0	66.9	47.6	49.8
Unknown	11.9	--	--	--	1.1	--	<1	<1	<1	<1	<1	<1	<1	<1
Tetrahydroabietic (?)	13.0	--	11.6	16.7	7.7	2.9	3.2	6.4	2.0	2.4	1.8	1.6	4.6	2.9
Pimaric	14.7	10.4	14.9	11.5	8.1	8.4	9.8	7.1	9.4	10.9	6.3	6.7	9.6	8.8
Sandaracopimaric	16.5	9.9	--	6.4	3.2	4.1	5.2	2.4	4.7	5.0	2.5	2.2	3.6	3.5
Dihydroabietic (?)	18.8	41.9	31.0	17.1	<1	3.9	1.2	<1	1.1	1.3	<1	1.0	<1	2.7
Palustric/levopimaric	20.1	--	--	--	1.6	--	--	1.4	--	--	1.9	2.2	1.1	1.0
Isopimaric	21.5	16.6	9.9	10.7	22.7	31.8	45.9	16.8	30.2	37.9	21.2	27.9	32.0	32.6
Unknown	25.7	--	<1	3.7	1.0	<1	--	1.1	1.5	1.4	3.2	1.3	1.3	<1
Abietic	31.4	<1	<1	4.7	39.2	10.4	11.1	42.1	9.5	10.7	38.3	43.1	27.8	29.1
Dehydroabietic	34.6	21.2	32.7	29.2	14.0	37.2	23.2	20.4	41.2	29.1	19.4	12.5	24.5	16.9
Neoabietic	36.8	--	--	--	1.7	<1	<1	1.0	<1	<1	2.5	1.5	<1	<1
Unknown	40.9	--	--	--	--	1.3	<1	--	<1	<1	<1	--	<1	<1
Dehydroabietic/ abietic ratio		21.2	32.7	6.2	0.34	3.68	2.09	0.49	4.34	2.72	0.51	0.29	0.88	0.58

[a] CTO was fractionated on DEAE-Sephadex and the acids were separated into fatty acids and resin acids by differential methylation.

[b] Percentage of CTO after purification of the methyl esters on alumina.

[c] Acids whose identity was uncertain are indicated by (?).

Another point of interest was the possible presence of resin acids in the aspen. Generally, resin acids are considered to be absent from hardwood extractives (5), but these results are consistent with the observation of Buchanan and coworkers (6) who cited the possible presence of resin acids in the extractives of paper birch. More recent reports by Cunningham and coworkers (7) described resin acids recovered from a tropical hardwood genus but the chemical nature of the components was not typical of temperate zone softwoods. Additional work on this project (data not shown) supported the possible presence of resin acids in aspenwood extracts, but the amounts were very small in proportion to the fatty acids, and would have little if any practical bearing on the recovery of tall oil from hardwoods.

The acid fractions were analyzed by gas chromatography and the results are listed in Table II. By inspection, the data showed that aspen was relatively high in linoleic acid in comparison with the fatty acids from the slash pine. Otherwise, the oxygen/sodium hydroxide cooking had very little effect on the survival of the fatty acids.

In the case of the resin acids, the survival was comparatively unaffected by the oxygen/sodium hydroxide except in the cooking of normal and "untreated" slash pine. In these cases the dehydroabietic acid tended to increase at the expense of abietic acid. These results were consistent with those observed previously (8) when sodium hydroxide with and without oxygen was used to cook loblolly pine.

These results led to a series of oxygen/sodium hydroxide experiments in which the amount of wood was varied from 0-40 g without changing other parameters. The details and results follow in the next part.

TALL OIL ACIDS COOKED WITH EXTRACTIVE-FREE LOBLOLLY PINE CHIPS IN OXYGEN/SODIUM HYDROXIDE

Three series of oxygen/sodium hydroxide cooks were run with extractive-free loblolly pine chips to which specific amounts of the refined tall oil acids were added. These experiments were designed to explore the possible "protective" action of the wood toward oxidation of the tall oil acids.

A. Tall Oil Fatty Acids

In the first series 1.35 g of tall oil fatty acids was added to 5, 10, 20, and 40 g of the extractive-free chips. The amounts of alkali and liquor were constant so that the digester with 5 g of wood carried an 8-fold excess of alkali-to-wood over the 40 g charge. The results, shown in Table III, indicated that the wood was severely attacked with a pulp yield of 5.2% for the 5-g charge of wood, while the crude tall oil (CTO) was recovered in a yield of 80% of the added acids. As the proportion of wood was increased, the recovery of crude tall oil increased although some scatter was evident. When the acid fraction of the CTO was recovered and analyzed, the data showed a general trend toward improved recovery with increased amounts of wood. Analysis of the acid fraction by gas chromatography showed clearly that the composition was changed in no major way due to oxygen/sodium hydroxide. However, the oleic acid/linoleic acid ratio showed that the attack on linoleic acid during the cooking process was reduced as the amount of wood increased.

The apparent "protective" action of the wood in this series prompted the omission of wood in one digester of the next series to test further this possible "protective" action.

TABLE III

TALL OIL FATTY ACIDS (1.35 G) COOKED WITH EXTRACTIVE-FREE LOBLOLLY PINE CHIPS IN OXYGEN/SODIUM HYDROXIDE[a]

Digester		B	D	F	G	
Extractive-free loblolly pine chips, g		5	10	20	40	
Yield of pulp, % of o.d. wood		5.2	12.3	31.8	55.7	
Total CTO, % of added fatty acids		79.8	89.2	96.8	92.8	
Fractionation of CTO on DEAE-Sephadex, % of CTO						
Neutrals		5.7	7.3	2.8	3.3	
Fatty acids		84.2	82.1	91.1	91.7	
Analysis of Acid Fractions by Gas Chromatography, % of fraction analyzed	Retention Time, min					Unitol Fatty Acids
Fatty acids						
Stearic	7.9	3.0	2.6	2.6	2.4	2.4
Oleic	9.4	60.8	55.8	54.1	53.1	51.0
Linoleic	12.0	26.7	30.9	33.9	35.8	38.5
C_{20} (?)	13.6	1.4	1.5	2.0	2.4	2.7
U (linolenic)	16.4	6.4	7.0	5.5	4.0	2.7
Unknown	19.4	<1	1.5	1.8	1.8	2.1
Oleic/linoleic acid ratio		2.28	1.81	1.60	1.48	1.32

[a]The liquor analyzed was the combined digester liquor and fiberized chip washings.

U = unknown.

B. Tall Oil Resin Acids

The experiment as described in Part A, above, was repeated except that resin acids were used in place of fatty acids, and wood was omitted from one digester. The results are listed in Table IV.

In the absence of wood (Digester B) 14% of the resin acids were recovered, but with only 5 g of wood at a pulp yield of 6.2%, the recovery of resin acids was 44%. With larger amounts of wood, 15 and 40 g, the recovery of resin acids was 51 and 57%, respectively. As with the fatty acids the survival of resin acids was strongly favored by the presence of wood.

The resin acid fractions were analyzed by gas chromatography and the results are shown in Table IV. The relative composition with respect to individual acids showed minor changes except for abietic and dehydroabietic acids. Expressed as a sum, abietic and dehydroabietic acids were the main part, 61-73%, of the resin acid fraction, while the ratio of dehydroabietic acid/abietic acid showed the marked increase in dehydroabietic acid at the expense of abietic acid. These data are consistent with (a) the general attack of oxygen/sodium hydroxide on the resin acids and (b) the considerable "protective" effect of wood on resin acid destruction. However, the "protective" effect of the wood may be regarded as a consequence of concurrent reactions with the attack on the tall oil acids somewhat slower than the attack on the main wood components, especially lignin.

In order to reinforce these observations a typical mixture of tall oil acids was chosen for a third series of oxygen/sodium hydroxide cooks in which both resin and fatty acids were added.

TABLE IV

TALL OIL RESIN ACIDS (1.35 G) COOKED WITH EXTRACTIVE-FREE LOBLOLLY PINE CHIPS IN OXYGEN/SODIUM HYDROXIDE[a]

Digester	B	D	F	G
Extractive-free loblolly pine chips, g	0	5	15	40
Yield of pulp, % o.d. wood	--	6.2	24.4	63.5
Apparent CTO, % of added resin acids	14	44	51	57
Fractionation of CTO on DEAE-Sephadex, % of CTO				
Neutrals	15.1	20.9	9.1	15.1
Resin acids	73.3	75.1	79.3	73.3

Analysis by GLC, % of fraction analyzed	Retention Time, min					Unitol Rosin, unsapfd.	Unitol Rosin, sapfd.
Unknown	10.6	<1	1.3	<1	1.0	<1	<1
Tetrahydroabietic	12.8	4.1	5.9	5.0	4.7	3.3	3.5
Pimaric	14.4	5.0	6.2	5.6	5.0	3.8	4.1
Sandaracopimaric	16.3	4.1	6.9	6.0	5.2	4.0	4.5
Dihydroabietic (?)	18.3	4.1	3.5	3.0	2.0	<1	1.6
Levopimaric/palustric	20.0	6.7	10.7	11.4	11.5	15.9	15.5
Isopimaric	21.2						
Unknown	23.2	<1	2.8	3.6	3.7	4.7	4.8
Unknown	25.8	<1	<1	<1	<1	1.4	1.6
Abietic	30.9	<1	8.7	19.0	26.3	39.2	39.2
		73.2	61.1	62.8	65.2	62.3	61.1
Dehydroabietic	34.1	73.2	52.4	43.8	38.9	23.1	21.9
Neoabietic	36.3	<1	<1	<1	<1	2.3	2.2
Unknown	39.8	1.8	1.1	1.0	<1	<1	<1
Dehydroabietic/abietic acid ratio		74.2	6.03	2.31	1.48	0.59	0.56

[a]Oxygen available: ca. 3.1 g or 0.1 mole. A charge of 5 g of wood requires ca. 0.2 mole of oxygen for the conversion of all the carbon-to-carbon dioxide. The amount of sodium hydroxide present was ca. 0.25 mole: FA or RA ≃ 0.0045 mole.

C. Tall Oil Fatty and Resin Acids, 1:1

The third experiment was similar to Part B, above, except that a 1:1 mixture of fatty and resin acids was used in place of the resin acids. The results are listed in Table V.

The yields of recovered acids and pulps were consistent with those observed in Parts A and B with wood exercising the usual "protective" action. With the fatty and resin acids present together, the fatty acids appeared to be somewhat more stable than the resin acids, an observation generally consistent with experiments (Parts A and B) in which the acids were cooked separately.

Based on the results of the above three series of cooks, tall oil acids may be expected to survive in substantial yields in oxygen/sodium hydroxide pulping under certain conditions (see below). Some losses may occur, especially of linoleic acid, and some abietic acid may be oxidized to dehydroabietic acid. However, at least two factors may have considerable influence on the yields and the nature of tall oil: (1) the efficiency of oxygen absorption and (2) the coarseness of the wood. In this work conventional chips were cooked in a digester where only a gentle sliding action of the charge was possible. The air in the digester was replaced with oxygen gas at 140 psig (ambient temperature) and no additional gas was added during the cook to replace that used in the reaction. Except for one attempt, no effort was made to determine residual oxygen at the end of the cook due chiefly to the limitations of available equipment. The residual oxygen in one experiment was approximately 55% of the original charge. The volume occupied was approximately 250 ml with the liquor and wood occupying the remainder, approximately 250 ml. In pulping equipment of other designs, especially where the cooking liquor may be sprayed through the gaseous oxygen at temperature (9,10) and where the pressure of oxygen is maintained, the possible destruction of tall oil components may be more extensive than in our process.

TABLE V

TALL OIL ACIDS (FATTY ACIDS/RESIN ACIDS, 1:1) COOKED WITH EXTRACTIVE-FREE LOBLOLLY PINE CHIPS IN OXYGEN/SODIUM HYDROXIDE

Digester		B	D	F	G	
Extractive-free loblolly pine chips, g		0	5	15	40	
Yield of pulp, % of o.d. wood		--	1.4	25.4	56.8	
Extracted CTO, % of added acids		17.2	56.0	61.4	62.6	
Fractionation of CTO on DEAE-Sephadex, % of CTO						
Neutrals		22.5	12.6	9.4	10.6	
Fatty acids		62.6	65.6	74.0	73.1	
Resin acids		12.2	20.7	17.3	23.9	
Analysis by GC, % of fraction analyzed[a]	Retention Time, min					Unitol Acids
Fatty acids						
Stearic	7.8	9.6	2.5	2.6	2.7	2.8
Oleic	9.3	84.8	62.9	56.6	53.5	53.1
Linoleic	11.8	2.2	19.7	26.6	34.1	38.4
C_{20}	13.3	<1	<1	1.6	2.6	1.8
Linolenic	16.3	<1	11.1	8.3	3.6	2.3
Unknown	19.2	<1	1.4	1.8	1.8	1.6
Unknown	21.1	1.3	<1	<1	<1	<1
Oleic/linoleic acid ratio		38.5	3.19	2.13	1.57	1.38
Resin acids						
Unknown	11.8	1.9	<1	<1	<1	--
Tetrahydroabietic	12.8	5.0	7.3	7.5	6.9	3.3
Pimaric	14.3	5.9	7.3	7.1	6.5	3.8
Sandaracopimaric	16.2	5.6	8.4	8.6	7.4	4.0
Dihydroabietic	18.3	4.2	2.9	2.7	2.5	<1
Palustric/ levopimaric	19.7	--	--	--	1.2	9.4
Isopimaric	20.9	6.1	10.7	11.7	10.3	6.5
Unknown	22.9	1.1	1.2	2.4	3.8	4.7
Unknown	25.0	--	--	--	1.1	1.4
Unknown	27.7	1.5	--	--	--	--
Abietic	30.5	<1	<1	3.9	11.1	39.2
Dehydroabietic	33.7	64.3 (65.3)	59.1 (60.1)	54.1 (58.0)	47.1 (58.2)	23.1 (62.3)
Neoabietic	36.0	--	--	--	--	2.3
Unknown	39.5	2.3	1.2	1.2	1.0	<1
Dehydroabietic/ abietic acid ratio		64.3	59.1	13.9	4.25	0.59

[a]Individual acids were identified presumptively by comparison with authentic compounds.

Comparisons were made between fiberized wood and chips in the survival of tall oil precursors. The results are described in the next section.

COOKS WITH FIBERIZED WOOD AND CHIPS IN SODIUM HYDROXIDE, WITH AND WITHOUT OXYGEN

One of the important factors in oxygen/alkali pulping is the form of wood most suited to acceptable yields of pulps which can meet specified paper-making properties. Toward this general objective various forms of fiberized wood are being studied in other laboratories to replace conventional chips which tend to cook nonuniformly (10-12).

For work on this project, one form of fiberized wood was prepared by steaming and then milling loblolly pine chips. Subsequently, batches of chips and fiberized wood were extracted with acetone and the extractive-free, air-dried wood was used in oxygen/sodium hydroxide cooks to which tall oil acids (or sodium salts) were added.

One series, as a control, was run with air sealed at atmospheric pressure. In another series oxygen gas at 140 psi was used in the usual way. The results of the two series are listed in Tables VI-VIII.

The differences in pulp yields were not significant despite the fact that the digester containing oxygen/alkali, fiberized wood, and fatty acids lost the oxygen gas through a defective seal and, therefore, was nearly identical with the control (essentially a sodium hydroxide cook with one atmosphere of air).

The yields of extractable crude tall oil (CTO) were generally consistent with those in other experiments. The form of wood, fiberized or in chips, was insignificant in air/sodium hydroxide in determining the yields of CTO which were nearly quantitative. However, in oxygen/sodium hydroxide cooks the yields

TABLE VI

TALL OIL ACIDS ADDED TO EXTRACTIVE-FREE LOBLOLLY PINE AND COOKED IN SODIUM HYDROXIDE, WITH AND WITHOUT OXYGEN[a]

Air/Sodium Hydroxide Cooks	Yield of Pulp, % of o.d. wood	From Filtrate				From Decanted Liquor, chips only				From Acidified Pulp				Total CTO and Acids			
		CTO		Acids by GC		CTO		Acids by GC		CTO		Acids by GC					
		g	Total CTO, %	g	CTO, %	g	Total CTO, %	g	CTO, %	g	Total CTO, %	g	CTO, %	g	CTO, % added acids	Acids, g	Acids, % CTO
Extracted fiberized wood																	
Fatty acids	67.5	0.543	93	0.435	80	--	--	--	--	0.042	7.3	0.0083	20	0.585	117	0.442	76
Resin acids	68.5	0.423	91	0.334	79	--	--	--	--	0.042	9.1	0.0059	14	0.466	93	0.340	73
Extracted chips																	
Fatty acids	68.0	0.074	17	0.049	66	0.408	80	0.367	90	0.028	5.5	0.0202	73	0.510	102	0.436	86
Resin acids	67.7	--[c]	--	--	--	0.249	--	0.189	76	0.017	--	0.0044	26	--	--	--	--
Oxygen/Sodium Hydroxide Cooks																	
Extracted fiberized wood																	
Fatty acids[b]	63.8	0.509	93	0.392	77	--	--	--	--	0.041	7.5	0.0043	10	0.550	110	0.396	72
Resin acids	57.9	0.192	84	0.105	55	--	--	--	--	0.039	17	0.0020	5	0.230	46	0.107	47
Extracted chips																	
Fatty acids	64.7	0.170	63	0.109	64	0.067	25	0.041	61	0.032	12	0.0219	68	0.269	54	0.172	64
Resin acids	62.3	0.135	56	0.060	44	0.073	30	0.032	45	0.034	14	0.0157	47	0.242	48	0.108	45

[a] In each digester 0.5 g of the acids was cooked with 20 g of acetone-extracted wood.

[b] Due to mechanical failure most of the oxygen leaked from the digester during the cook.

[c] Filtrate and washings lost by accident.

TABLE VII

RELATIVE COMPOSITION BY GAS CHROMATOGRAPHY OF EXTRACTED CRUDE TALL OIL (CTO)

Fatty Acids Added to Extractive-free Loblolly Pine, and Cooked with Sodium Hydroxide in Air and in Oxygen (Table VI)

Substance Found[a]	Retention Time[b], min		In Air					In Oxygen					Stock Solution of Fatty Acids
			With Fiberized Wood		With Chips			With Fiberized Wood		With Chips			
	Col. Temp., 200°C	Col. Temp., 174°C	Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	
C_{15}	1.8	3.7	t	t	t	t	0.3	t	1.7	t	t	0.36	t
Palmitic (C_{16})	2.2	4.8	t	1.3	0.8	t	0.9	t	2.3	0.9	t	0.55	t
Stearic (C_{18})	3.6	7.8	2.0	3.3	1.3	1.9	4.0	2.3	5.8	3.4	2.3	2.9	2.2
Oleic	4.2	10.2	50.6	67.7	41.8	51.7	74.2	52.7	67.9	63.3	63.7	64.0	52.1
C_{19}	4.6	11.6	t	1.7	t	t	1.2	t	t	t	t	1.14	t
Linoleic	5.2	13.0	28.9	13.2	32.6	25.3	6.6	33.0	16.2	27.0	28.9	27.0	38.0
C_{20}	5.8	14.5	1.4	--	1.9	0.7	0.6	1.9	t	1.8	1.9	1.4	2.3
Linolenic	6.8	18.0	12.7	9.2	12.7	14.1	9.2	6.3	4.7	1.9	1.0	1.9	2.1
Unknown	7.6	21.0	4.5	2.4	5.3	4.8	1.4	2.6	1.5	1.8	0.9	0.7	2.1
Unknown	8.5	--	t	--	1.2	0.9	--	0.8	--	t	t	--	0.7
Unknown	9.6	--	t	--	0.6	0.6	--	0.5	--	t	t	--	0.6
Oleic/linoleic ratio			1.75	5.13	1.28	2.04	11.3	1.59	4.18	2.34	2.21	2.37	1.37

[a] Individual acids were identified presumptively by comparison with known acids.

[b] The data in the table were determined from chromatograms obtained at two column temperatures, 174°C and 200°C.

t = trace.

TABLE VIII

RELATIVE COMPOSITION BY GAS CHROMATOGRAPHY OF EXTRACTED CRUDE TALL OIL (CTO)

Resin Acids Added to Extractive-free Loblolly Pine and Cooked with Sodium Hydroxide in Air and in Oxygen (Table VI)

Substance Found[a]	Col. at 200°C Retention Time, min	In Air					In Oxygen					Stock Solution of Resin Acids
		With Fiberized Wood		With Chips			With Fiberized Wood		With Chips			
		Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	
Fatty acids	1.7-9.8	2.8	31.8		1.4	24.4	2.1	49.1	5.0	2.1	8.2	1.8
Resin acids												
Dehydroabietic (isomer)	11.8	2.8	t		2.9	3.8	4.2	5.6	3.2	2.7	3.2	3.1
Tetrahydroabietic (isomer)	13.2	5.5	7.3		5.3	11.2	8.3	9.4	7.0	7.2	8.1	5.6
Pimaric	14.8	4.7	4.6		4.3	10.2	6.7	--	4.3	3.9	7.7	5.4
Sandaracopimaric	16.7	1.3	7.0		1.5	2.8	1.5	14.1	1.4	1.4	2.6	1.8
Levopimaric/palustric	18.2	8.3	--		7.4	--	--	7.2	--	--	--	7.5
Isopimaric	19.0	6.0	5.6		6.3	11.3	8.6	--	6.3	5.5	10.2	7.1
Unknown	21.1	3.4	1.4		3.5	3.7	1.3	--	0.9	t	1.2	3.4
Unknown	22.9	1.1	--		1.4	t	0.5	--	t	--	--	1.1
Abietic	27.7	28.8	13.7		28.0	13.8	2.4	3.1	1.2	t	3.1	23.6
Dehydroabietic	30.4	34.0	21.8		36.3	17.4	61.8	12.0	69.6	75.7	55.7	38.1
Neoabietic	32.5	0.6	--		0.8	--	--	--	--	--	--	0.4
Unknown	35.2	0.8	--		0.6	--	2.6	--	1.3	1.6	--	0.4
Dehydroabietic/abietic ratio		1.18	1.59		1.30	1.26	25.8	3.87	58.0	75.7[b]	18.0	1.62

Sample not available for analysis

[a] Individual acids were identified presumptively by comparison with known acids.

[b] This ratio calculated with the amount of abietic acid set arbitrarily at 1%.

t = trace.

of CTO were approximately half those in air/alkali cooks (Table VI). Furthermore, the amount of CTO recovered from the liquor decanted from chips was much smaller than from corresponding liquors with air/alkali. Although these results appeared to contradict an earlier result in which very little if any loss of CTO occurred (1), differences in the experimental conditions may account for the lower yield. Thus, in the initial work (1), the liquor/wood ratio was 3.85; in these studies the ratio was 10. Also, the digester charges were smaller in the later experiments which provided for proportionately larger amounts of oxygen. The combined result of these changes may have exposed the tall oil components to more oxidation (destruction) than in the earlier cooks. Finally, the results of these studies may be subject to considerable scatter (experimental variability) due to other unidentified factors. More closely controlled statistically-valid experiments would be required to test this notion.

The results of the analysis of the acid fractions by gas chromatography are summarized in Tables VII and VIII.

Except for the acids extracted from the pulps, the distributions of component acids resembled the distribution in the original tall oil fatty acid mixture (Table VII). The acids extracted (by acetone) from the acidified pulps, although representing a small fraction of the total tall oil, appeared to be somewhat more highly oxidized than corresponding fractions in the same cook. Thus, the oleic/linoleic acid ratios of the CTO were considerably larger for the pulps than for the liquors due to loss of more linoleic than oleic acid. Such losses may be due to oxidation by air during the interval between the recovery of the wet pulp and the extraction with acetone. However, no definitive data were sought on this point.

The results of the analysis by gas chromatography of the acid fractions from the resin acid cooks are listed in Table VIII.

As in previous experiments (1) the dehydroabietic acid/abietic acid ratios were approximately unchanged for the air/sodium hydroxide cooks, but the oxygen/sodium hydroxide system changed nearly all the abietic acid to dehydroabietic acid. Otherwise, general oxidation of all components appeared to contribute to the reduced yields of extractable tall oil.

TALL OIL ACIDS COOKED WITH FIBERIZED RED MAPLE IN OXYGEN/SODIUM HYDROXIDE

Fiberized red maple, which had been treated with alkali before mechanical fiberization, was available from Dr. Gordon Nicholls, Project 3264. A series of four oxygen/sodium hydroxide cooks was run with tall oil fatty and resin acids and the fiberized red maple to test the possible protective action of such fiberized wood in oxygen/alkali pulping. The results are listed in Table IX.

The fatty acids in the control (digester B) were present in small amounts and, no doubt, represent only an unknown portion of those originally present. The resin acid content was negligible (5,6). By inspection of the extracted crude tall oil yields for digesters D, F, and G, the protective action of the wood appeared to be substantial. Furthermore, the ratios of dehydroabietic/abietic acids suffered only minor shifts in comparison with the corresponding ratios in similar cooks using loblolly pine (see Tables V and VIII). However, the protective action of wood toward the destruction of tall oil acids appears to be substantial but the data are scattered and conclusions are difficult to draw.

TABLE IX

TALL OIL FATTY AND RESIN ACIDS COOKED WITH FIBERIZED RED MAPLE IN OXYGEN/SODIUM HYDROXIDE[a]

Digester	B	D	F	G
Acids added	None (control)	1.35 g fatty acid	1.35 g resin acids	1.35 g fatty and resin acids 1:1
Yield of pulp, % o.d. wood	16.5	15.5	18.0	16.5
Total apparent CTO, % of added acids	(0.086 g)[b]	96.4	83.1	89.5
Fractionation of CTO on DEAE-Sephadex, % CTO				
Neutrals	81.7	4.8	18.8	7.7
Fatty acids	18.3	92.2	--	56.5
Resin acids	--	--	79.1	33.2

Analysis by GLC, % of fraction analyzed[c]	Retention Time, min					Unitol Fatty Acids
Fatty acids						
C_{15}	3.3	11.0	1.1		1.3	1.3
Palmitic	4.4	10.0	<1		1.2	<1
Palmitoleic	5.4	<1	<1		<1	<1
C_{17} (standard)[d]	5.9	(18.2)	(25.0)		(25.1)	(25.0)
Stearic	7.9	4.6	2.4		3.0	2.6
Oleic	9.3	17.8	53.0		49.2	49.3
C_{19}	10.5	3.9	<1		1.4	1.0
Linoleic	11.8	6.2	32.0		27.6	37.9
C_{20}	13.4	--	1.2		2.2	3.2
Linolenic	16.4	8.5	6.9		9.5	2.6
Unknown	17.8	--	--		1.6	<1
Unknown	19.5	38.4	1.9		3.0	2.0
Oleic/linoleic acid ratio		2.87	1.65		1.78	1.30
Resin acids						Westvaco Resin Acids
Unknown	10.6			1.6	<1	<1
Dihydroabietic (isomer)	11.9			<1	<1	--
Tetrahydroabietic	12.8			3.1	3.7	2.1
Pimaric	14.3			5.8	5.4	4.3
Sandaracopimaric	16.1			5.5	6.0	3.7
Dihydroabietic (isomer)	18.0			2.7	1.7	1.3
Palustric/levopimaric	19.8			5.8	3.3	9.8
Isopimaric	20.9			6.5	6.6	5.6
Unknown	22.8			3.3	4.1	2.7
Unknown	25.0			1.8	2.0	<1
Abietic	30.4			25.8	28.2	36.6
Dehydroabietic	33.4			35.7	36.9	30.5
Neoabietic	36.0			1.2	1.3	1.6
Unknown	39.1			1.0	1.8	<1
Dehydroabietic/abietic acid ratio				1.38	1.31	0.83

Not analyzed[e]

[a] Alkali-pretreated, fiberized red maple, 20 g, was cooked in oxygen/sodium hydroxide, 22% NaOH on a wood basis, 140 psi of oxygen gas, and two hours at 160°C.
[b] CTO from 20 g of fiberized red maple.
[c] Heptadecanoic acid, $C_{16}H_{33}CO_2H$, used as standard.
[d] Amount added as % of CTO.
[e] Chromatograms contained unidentified peaks.

TALL OIL ACIDS COOKED WITH EXTRACTIVE-FREE LOBLOLLY PINE IN OXYGEN/SODIUM CARBONATE AND OXYGEN/SODIUM BICARBONATE

A series of four cooks was run with extractive-free loblolly pine fiberized wood and chips. Oxygen/sodium carbonate and bicarbonate were used to cook a synthetic mixture of fatty and resin acids in a 1:1 ratio by weight. The results are listed in Table X.

The yields of pulp were similar to those in oxygen/sodium hydroxide pulping (Table VI) with somewhat lower yields with fiberized wood than with chips. However, the yields of extractable tall oil were relatively insensitive to the form of the wood, as observed previously, and were less than half the amount of added tall oil acids. This result is similar to that with oxygen/sodium hydroxide (see Table VI).

Analysis of the acid fractions by gas chromatography revealed a considerable increase in the oleic/linoleic acid ratio which was consistent with that when considerable oxidation had occurred. The most dramatic effect, however, was the absence of abietic acid indicating a complete conversion to dehydroabietic acid. This result may be consistent with a hypothesis of Thompson (14) who proposes that the active oxidant is different and possibly more active, toward certain chemical groups, in oxygen/sodium carbonates than in oxygen/sodium hydroxide. The lowered yield is consistent with a general oxidative attack on the tall oil acids.

TALL OIL ACIDS COOKED IN OXYGEN/CARBONATE SYSTEMS WITH VARYING AMOUNTS OF EXTRACTIVE-FREE, FIBERIZED LOBLOLLY PINE

When tall oil acids were cooked with varying amounts of wood in oxygen/sodium hydroxide, the wood was attacked preferentially. This resulted in disproportionately large recoveries of extractable crude tall oil (CTO) when compared

TABLE X

RECOVERY AND ANALYSIS OF CRUDE TALL OIL FROM CARBONATE/OXYGEN AND BICARBONATE/OXYGEN COOKS

Type of cook	In Oxygen/Sodium Carbonate					In Oxygen/Sodium Bicarbonate						
Form of extractive-free wood	With Fiberized Wood		With Chips			With Fiberized Wood		With Chips				
Yield of pulp, % o.d. wood	65		74			61		70				
Total CTO recovered based on added acids, %	44.7		42.6			43.4		51.1				
Combined fatty and resin acids, % of CTO	45.1		58.5			56.3		63.2				
Analysis of CTO Acids by GLC[a]	Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	Filtrate and Washings	Pulp	Filtrate and Washings	Decanted Liquor	Pulp	Stock Solutions Fatty Acids	Stock Solutions Resin Acids
Fatty and resin acids combined as % of CTO in fraction	48.3	16.2	58.1	55.2	60.7	58.0	23.8	65.0	60.5	65.5	86.2	68.3
Chief individual acids relative to C_{17}-acid as internal standard, %												
Stearic	2.6	10.9	3.2	2.7	3.4	2.9	13.1	2.3	2.3	2.7	1.9	t
Oleic	44.0	55.3	46.3	42.5	55.7	46.8	61.0	45.7	43.8	56.7	54.6	t
Linoleic	4.8	1.7	9.9	9.7	11.4	8.1	3.4	12.6	13.2	12.9	40.8	t
Oleic/linoleic ratio	9.2	3.2	4.7	4.4	4.9	5.8	17.9	3.6	3.3	4.5	1.34	--
Dehydroabietic[b]	32.2	8.2	28.2	30.5	12.4	31.4	6.6	23.7	34.0	13.1	--	29.2[c]

[a] Internal standard was $C_{16}H_{33}CO_2H$.

[b] The abietic acid peak was absent from all chromatograms except the stock solution of resin acids.

[c] Abietic acid content 35.0%.

t = trace.

with pulp yields (see Tables III-V). Guided by these experiments with oxygen/sodium hydroxide, a series of cooks was made with extractive-free, fiberized loblolly pinewood in oxygen/sodium carbonate and in oxygen/sodium bicarbonate, and the results are summarized in Tables XI and XII.

By inspection of Tables V and XI, the yields of pulp were somewhat larger in the presence of sodium carbonate than with sodium hydroxide. However, the yields of CTO followed a different pattern for the carbonate than for the hydroxide cooks. Although the data have little statistical value, the trends, qualitatively, appear to be real with the 5-g charge of wood yielding the most CTO. Furthermore, the action of oxygen in the presence of carbonate may involve a mechanism different from that when hydroxide is the base as suggested by Thompson (14). This possibility may be supported, also, by the complete disappearance of abietic acid with a corresponding increase in the proportion of dehydroabietic acid.

When the tall oil acids were cooked in oxygen/sodium bicarbonate, Table XII, the yields of CTO were lowest of the three oxygen/alkali systems. Again, the 5-g charge of wood gave the highest yield of CTO; Pulp yields, on the contrary, were highest. Other differences in behavior included the oleic acid/linoleic acid and the dehydroabietic acid/abietic acid ratios. An inspection of these ratios reveals that the severity of attack on tall oil components increased in the order (as sodium compounds): hydroxide < carbonate < bicarbonate. On the other hand, pulp yields appeared to follow the reverse order with oxygen/sodium hydroxide producing the lowest yields. Although these results are somewhat scattered, they seem consistent with reaction mechanisms which are dependent upon the type and concentration of anion as well as the alkalinity (14).

TABLE XI

TALL OIL ACIDS COOKED WITH VARYING AMOUNTS OF EXTRACTIVE-FREE, FIBERIZED LOBLOLLY PINE BY THE OXYGEN/SODIUM CARBONATE PROCESS

Digester	B	D	F	G			
Amount of wood, g	0	5	10	20			
Yield of pulp, % o.d. wood[a]	--	20	42	64			
Total CTO based on tall oil acids added to the wood, %		69.7	40.2	41.8			
Relative Composition, %, by Gas chromatography, internal standard C_{17}-acid[b]					Fatty Acid Stock Solution	Rosin Acid Stock Solution	Composition Adjusted to FA/RA, 1:1, %
Stearic	3.6; 3.5	2.0; 2.2	3.4	2.5	1.8	--	0.9
Oleic	48.7; 50.1	45.9; 46.6	49.1	43.7	53.2	--	26.6
Linoleic	11.7; 11.4	20.5; 20.8	10.4	9.5	39.0	--	19.5
Oleic/linoleic acid ratio	4.2; 4.4	2.2; 2.2	4.7	4.6	1.36	--	1.36
Abietic	--	--	--	--	--	34.5	17.3
Dehydroabietic	27.6; 28.4	19.4; 21.4	24.5	31.8	--	29.9	15.0

[a]The pulp from Digesters D and F were relatively high brightness; the pulp from Digester G was red-brown in color.

[b]Only the main components are listed.

TABLE XII

TALL OIL ACIDS COOKED WITH VARYING AMOUNTS OF EXTRACTIVE-FREE, FIBERIZED LOBLOLLY PINE BY THE OXYGEN/SODIUM BICARBONATE PROCESS

					Fatty Acid Stock Solution	Resin Acid Stock Solution
Digester	B	D	F	G		
Amount of wood, g	0	5	10	20		
Yield of pulp, % o.d. wood[a]	--	56.4	65.1	67.5		
Total CTO based on tall oil acids added to the wood, %	7.3	44.8	34.1	31.9	86.6	74.0
Analysis by Gas Chromatography[b]						
Relative composition, % of acids in CTO from filtrate and washings						
Fatty acids						
Stearic	11.5	3.6	3.7	3.4	2.24	
Oleic	17.7	56.8	59.9	49.3	52.8	
Linoleic	t[d]	9.8	6.9	4.6	38.0	
Oleic/linoleic ratio	17.7[c]	5.80	8.66	10.7	1.39	
Resin acids						
Abietic	nil	nil	nil	nil		15.1
Dehydroabietic	39.2	23.7	25.7	26.3		49.2

[a] The pulp from Digester D was light tan in color; those from Digesters F and G were brown.

[b] Only the main components are listed.

[c] The ratio was based arbitrarily on >1% for linoleic acid.

[d] t = trace.

POSSIBLE FATE OF TURPENTINE IN OXYGEN/ALKALI PULPING

Although the recovery of turpentine from the oxygen/alkali pulping of coniferous woods may be accomplished in preoxygen stages, an attempt was made on this project to explore the fate of turpentine in the oxygen/alkali cooking stage. Toward this objective two main series of experiments were performed.

Turpentine Recovered from Oxygen/Sodium Hydroxide Pulping

As shown in Table XIII, turpentine was recovered from oxygen/sodium hydroxide cooks in the absence of wood and from those with normal and resin-soaked wood. The turpentine was collected by a steam distillation method (18) and analyzed by gas chromatography. The results are listed in Table XIII. It seems noteworthy that turpentine was recovered in yields of 19-38% and that the composition was not changed in any major way. This was indicated by the α-pinene/β-pinene ratios which were diminished slightly in comparison with unoxidized starting materials.

In keeping with the tall oil studies, data for turpentine recovery and analysis were obtained also for the oxygen/carbonate systems.

Turpentine Recovered from Oxygen/Sodium Carbonate and Bicarbonate Pulping

A series of cooks with extractive-free wood and added amounts of sulfate turpentine was run with amounts of sodium carbonate and bicarbonate equivalent to the sodium hydroxide. The data for the recovery and analysis of the turpentine are listed in Tables XIV and XV. In comparison with the oxygen/sodium hydroxide cooks, the yields of turpentine were approximately one-half. The composition again reflected general oxidation with α-pinene slightly more reactive than β-pinene. However, aside from the impractically low yields, the quality of turpentine appeared to be equivalent to that of sulfate turpentine. Losses of 60-90% presumably would preclude the practical recovery of turpentine from oxygen/alkali pulping.

TABLE XIII

FATE OF TURPENTINE IN OXYGEN/SODIUM HYDROXIDE PULPING[a]

Digester	B	F[b]	D	G[b]
Wood	None	20 g loblolly pine chips	5 g slash pine lightwood	5 g lightered wood + 15 g extractive-free loblolly pine
Sulfate turpentine, crude	0.10 g	0.10 g	None	None
Yield of turpentine by GC, %	29.5	37.6	37.0[c]	18.5[c]
Turpentine analysis, relative composition by GC, %				
α-Pinene	60.7	62.2	42.8	40.9
β-Pinene	19.3	18.0	48.8	44.8
Δ^3-Carene, α-Phellandrene	8.2	6.7	--	--
Limonene, β-Phellandrene	4.0	3.6	1.4	3.1
High boiling point compounds	6.8	7.6	6.3	10.1
α-Pinene/β-pinene ratio	3.15	3.46	0.877	0.913

[a]Each digester contained 200 ml of 0.55N sodium hydroxide, was pressurized with oxygen to 140 psig, and was heated to 160°C for 2 hr.

[b]These digesters appeared to have lost pressure during the cook.

[c]Yields were based on 290 mg of turpentine/5 g of lightwood.

TABLE XIV

FATE OF TURPENTINE (0.10 G) WITH EXTRACTIVE-FREE LOBLOLLY PINE CHIPS (20 G) IN OXYGEN/SODIUM CARBONATE AND OXYGEN/SODIUM BICARBONATE COOKS

	Oxygen/Sodium Carbonate, 5.83 g Na_2CO_3 in 200 ml, 0.55N		Oxygen/Sodium Bicarbonate, 9.24 g $NaHCO_3$ in 200 ml, 0.55N	
Digester:	D	F	B	G
Yield of turpentine by GC, %	8.5	12.5	8.2	9.6
Turpentine analysis, relative composition by GC, %				
α-Pinene	38.0	54.4	53.1	63.8
β-Pinene	11.0	16.2	14.6	15.3
High boiling compounds	48.9	24.4	26.4	16.3
α-Pinene/β-pinene ratio	3.47	3.36	3.64	4.18

TABLE XV

RECOVERY OF TURPENTINE FROM LIGHTERED WOOD BY DISTILLATION WITH STEAM FROM AQUEOUS SODIUM HYDROXIDE

Experiment	I	II	III	IV	V	Sulfate Turpentine[b]	
						Date Anal., 6-17-76	Date Anal., 7-9-76
Lightered wood, g[a]	100	20	5	5	20		
Water for distillation, ml	700	140	200	200	25 ml H_2O + 140 ml ethylene glycol		
Sodium hydroxide added, g	28.0	5.6	4.0	4.0	5.6		
Distillation time, hr	2.5	4	3.5	3.5	2		
Yield of turpentine, g/100 g wood	5.03	5.72	5.84	6.47	5.45		
Turpentine Analysis, relative composition by GC, %							
α-Pinene	42.5	42.9	47.0	44.6	45.0	71.0	70.1
β-Pinene	45.8	46.5	46.2	48.1	46.2	16.3	15.5
Limonene + β-Phellandrene	4.6	4.9	3.5	3.6	4.6	3.1	3.7
High boiling compounds	5.9	4.5	2.7	2.5	2.5	2.2	2.5
α-Pinene/β-pinene ratio	0.932	0.923	1.017	0.929	0.975	4.53	4.34

[a] Small chips (1 × 5 × 10 mm) were cut by hand from a section of resin-soaked wood (Paraquat-treated slash pine).

[b] Approximately 5% of Δ^3-carene was present in addition to the analysis as tabulated.

EXPERIMENTAL

PULPWOOD SAMPLES

Loblolly Pine

Loblolly pinewood bolts were supplied by Champion International in Canton, North Carolina. This is the same wood that is being used in the concurrent Funded Formal Project 3264 on oxidative pulping and Project 3267 (Final Report dated August 9, 1976) on the maximization of tall oil soaps.

Trembling Aspen

Trembling aspen logs were supplied by Wausau Paper Mills Company from their forest in the vicinity of Rhinelander, Wisconsin.

Paraquat-treated Slash Pine

Bolts of normal and Paraquat-treated (3) slash pine were supplied by Mr. William Peters of the U.S. Forest Service from trees cut in the Owens-Illinois, Inc. forest near Olustee, Florida.

Production of Chips for Pulping

The loblolly pinewood and the aspenwood were chipped in a mechanical chipper to produce commercial-type chips. The slash pinewood was cut into disks which were chipped by hand with a hinged knife. In the case of the Paraquat-treated slash pinewood, the resin-soaked portions were separated from the disks before chipping.

Steamed and Fiberized Loblolly Pine Chips

A quantity of loblolly pine chips (see above) was steamed at 80 psi and the hot chips were fiberized in a 36-inch Bauer pulper with B957 plates set at 0.030-inch clearance. The fiberized wood was air dried and stored in the cold room.

Alkali-impregnated and Fiberized Loblolly Pine Chips

As requested by Dr. Gordon Nicholls, a quantity of loblolly pine chips (see above) was impregnated with a sodium hydroxide solution, steamed, and fiberized in a special mill at the Bauer Bros. Co., Springfield, Ohio. The chips, 75 lb o.d. (142.6 lb undried), were impregnated with a solution of 30.5 lb of sodium hydroxide dissolved in 79.4 gal of water. The surplus impregnation liquor, 73.4 gal, d. = 1.0389 g/ml, solids content 4.56%, was drained from the chips which were steamed and fiberized without further removal of liquor. Upon thorough washing, an aliquot of the fiberized wood gave an ovendry yield of 87%, based on the original o.d. wood.

The crude tall oil (CTO) was determined in the liquor, 0.64%, and in the fiberized wood, 0.68%, for a total of 1.32% based on the o.d. wood. No further work was done with this form of fiberized wood.

TALL OIL ACIDS

Refined tall oil acids were obtained from the Union Camp Corporation, Jacksonville, Florida and were analyzed by the procedure of Zinkel (16). The results are shown in Tables III-V and in Appendix III, Tables XVII-XIX.

Refined tall oil rosin was furnished by Westvaco, Charleston, South Carolina. An attempted purification and analysis are listed in Table XVI.

SULFATE TURPENTINE

Crude sulfate turpentine was furnished by the Thilmany Pulp and Paper Co., Kaukauna, Wisconsin (Division of Hammermill Paper Company).

TABLE XVI

ANALYSIS OF FRACTIONS IN ATTEMPTED PURIFICATION OF RESIN ACIDS FROM ROSIN (WESTVACO)

Solvent used for extraction	Retention Times, min	Sodium Resinate, ppt.		Filtrate (Mother Liquor) from Ppt.		Washings (Dilute NaOH) of Ppt.
		Ethyl ether	Petroleum ether	Ethyl ether	Petroleum ether	Ethyl ether
Yield (gravimetric) of resin acids recovered by acidification and extraction, % of rosin		95.6	94.4	1.1	0.33	0.47
Recovery by GC based on C_{17}-internal standard, % of solids in fraction		89.0	89.2	78.9	--	88.2
Analysis by GC, % of fraction analyzed						
Resin acids						
Unknown	10.4	<1	1.1	Not analyzed	--	--
Tetrahydroabietic (isomer)	12.6	2.3	2.7		1.9	1.3
Pimaric	14.2	4.3	4.8		3.2	3.9
Sandaracopimaric	16.0	4.0	4.3		<1	<1
Dihydroabietic (isomer)	18.8	1.5	1.6		<1	<1
Palustric/levopimaric	19.6	10.0	10.7		3.7	1.3
Isopimaric	20.7	5.6	5.3		1.9	1.8
Unknown	22.8	3.2	3.2		1.4	<1
Unknown	25.0	1.0	1.2		<1	<1
Abietic	30.3	34.7	36.2		14.9	15.7
Dehydroabietic	33.4	30.3	26.1		71.5	73.7
Neoabietic	35.5	1.7	2.5		--	--
Unknown	39.0	<1	<1		1.1	1.5

PULPING EQUIPMENT AND CONDITIONS

All pulping was done in stainless steel cylindrical digesters 53 mm in inside diameter by 240 mm in height and 3.5 mm wall thickness, and 530 ml volume. Each digester was closed by a two-piece threaded cap sealed with a Teflon ring gasket. As many as seven such units can be mounted in a rotating rack and immersed in an electrically-heated oil bath. Four of the units were equipped with valves for degassing and for pressurizing with gases.

DETERMINATION OF TALL OIL

The procedure described by Saltsman and Kuiken (15) was used to isolate the crude tall oil from pulping and washing liquors. The crude tall oil was separated into unsaponifiables, fatty acids, and resin acids by the procedure of Zinkel (16).

ANALYSIS OF TALL OIL FRACTIONS BY GAS CHROMATOGRAPHY

Benzene solutions (1%) of the methyl esters of fatty and resin acids were injected onto a column (6 ft x 1/8 inch, stainless steel) packed with 10% EGSS-X, at a temperature of 180°C for fatty acid esters and 200°C for resin acid esters. A hydrogen flame ionization detector was used with helium carrier gas in the column at 25 ml per minute.

Individual components were identified presumptively by relative retention times and by comparative behavior with authentic references. Quantitative analyses were based on the use of margaric acid, $C_{16}H_{33}CO_2H$, as an internal standard (20).

RECOVERY OF TALL OIL FROM PULPS

The recovery of tall oil from pulps was based on a general method outlined by Laundrie and Zinkel (17). After the fiberizing liquor was filtered from the pulp, the pad was washed and pressed as free of wash liquor as possible under a rubber sheet. The wet pad was broken by hand and was leached overnight with 125 ml of an acetone solution of sulfuric acid (20 ml of 5N aqueous sulfuric acid and 100 ml of water diluted to 1000 ml with acetone). The mixture was filtered on a sintered glass funnel and washed with 200 ml of fresh acetone applied in 50-ml portions. The pulp mat was pressed with a rubber sheet and oven dried for the determination of pulp yield. The combined acetone extract and washings were diluted with 100 ml of water, the acetone was evaporated at reduced pressure, and the residual mixture was analyzed for CTO.

COOKING TALL OIL ACIDS AND WOOD IN SODIUM HYDROXIDE,
WITH AND WITHOUT OXYGEN, A GENERAL PROCEDURE

With minor modifications the procedure described herewith was used in the pulping studies on Project 3266.

Loblolly pine in the form of chips and fiberized wood was extracted with acetone. The airdry wood, 20 g of either chips or fiberized wood, was placed in a 0.5-liter stainless steel digester. Either tall oil fatty or resin acids, 0.5 g, was added as an aqueous solution of sodium salts followed by an aqueous solution of sodium hydroxide containing 4.4 g as NaOH (22% on an airdry wood basis). Sufficient water was added to yield a total of 200 ml of cooking liquor or a liquor-to-wood ratio of 10:1. The digesters were sealed, one series was cooked with one atmosphere of air and the other with 140 psi of oxygen gas. The digesters were rotated slowly in an oil bath and held at 160°C for 120 min. The digesters were

removed from the oil, cleaned in a steam bath, and cooled to 90°C at which temperature they were opened. Those containing fiberized wood were emptied onto a sintered glass funnel and washed portionwise with hot water to yield 800-900 ml of liquor and washings combined. Digester liquor was decanted from cooked chips which were fiberized in a Waring Blendor in hot water, the slurry was filtered on the sintered glass funnel, and the pad of pulp was washed with small portions of hot water. The combined fiberizing liquor and washings, about 700 ml, was analyzed separately for CTO. The pulps from all cooks were analyzed for CTO, and the data from the two series are summarized in Tables VI and VII.

TALL OIL ACIDS COOKED WITH WOOD IN OXYGEN/CARBONATE SYSTEMS

The general procedure described above was used in the oxygen/carbonate cooks and the amount of sodium was held constant. Thus, the amount of sodium hydroxide was 22%, based on the o.d. wood, while sodium carbonate was 27% and sodium bicarbonate was 46% on the same basis. The data are listed in Tables X-XII.

DETERMINATION OF TURPENTINE IN WOOD AND BLACK LIQUOR

A. By Distillation from Aqueous Alkali

Based on a process described by Drew (18) an analytical procedure was devised for the determination of turpentine in wood (in the form of chips, fiberized wood or pulp) and in black liquor. A sample of wood or liquor was placed in a 1-liter round-bottomed flask equipped with a lighter-than-water solvent trap and a condenser. Wood samples were suspended in 0.5-1.0N sodium hydroxide and liquor samples, if necessary, were adjusted to pH >10 with sodium hydroxide. An amount of 3-7 ml of cyclohexane was placed in the flask and the

contents were heated sufficiently to produce a slow rate of reflux. The hydrocarbon solvent collected in the trap along with aqueous condensate. After three hours' heating, the trap was cooled, the solvent layer containing the turpentine was withdrawn through a small charge (2-3 g) of anhydrous sodium sulfate into a volumetric flask. The trap was washed with 1-2 ml of fresh solvent and the combined extract was adjusted to 5 or 10 ml in the volumetric flask. The solution of turpentine was analyzed by gas chromatography. The components were identified presumptively by retention times and by comparison with authentic compounds. The results are summarized in Tables XIII-XV. In Table XV are listed analytical data for lightered wood and for sulfate turpentine.

B. By Distillation from Aqueous Ethylene Glycol Containing Alkali

Attempts were made to determine turpentine in wood and pulp samples by a modification of a procedure developed by Drew and Pylant (19). The procedure as described under the previous heading was used for 50-g samples of wood and pulp except that the sample was suspended in a mixture of 25 ml of water and 75-100 ml of ethylene glycol containing 6.0-8.0 g of sodium hydroxide. The mixture was heated to boiling and the temperature (of the mixture) was adjusted to 140°C by the removal of the aqueous phase from the trap or by the addition of small amounts of water through the condenser. After 2-2.5 hours' refluxing, the turpentine solution (hydrocarbon layer) was analyzed as in the previous paragraph. For small samples the precision and accuracy were poor, and the method was dropped.

OXYGEN/SODIUM HYDROXIDE COOKING OF LIGHTERED WOOD, AND WITH EXTRACTIVE-FREE WOOD, WITH AND WITHOUT TURPENTINE

In a series of cooks, crude sulfate turpentine was cooked in oxygen/alkali at 160° for two hours as described in the tall oil experiments above.

Additional cooks were run with lightered wood, with and without added extractive-free wood. In the turpentine experiments the pressure in each digester was raised to 140 psi with oxygen (without the removal of air under vacuum). At the end of the cook, the digesters were cooled to the temperature of cold tap water, opened, and the contents transferred to the distillation flask to avoid losses by vaporization. The turpentine was collected and analyzed as described under the heading "Distillation from aqueous alkali" and the results are summarized in Table XIII.

AN IMPROVED METHOD OF SELECTIVE METHYLATION OF FATTY AND RESIN ACIDS WITH METHANOLIC HYDROGEN CHLORIDE

The selective esterification of fatty acids using methyl-sulfuric acid under reflux conditions proved to be unsatisfactory. Increasing the reaction time did not give complete reaction of the fatty acids, but initiated the esterification of resin acids after 15 min.

A slight modification of the method described by Balder and Crowell (20) using an esterification with methanolic hydrogen chloride at room temperature has been adapted to our method of analysis of fatty and resin acids. Not only has the completeness of fatty acid esterification improved, but the composition of the resin acid fraction at the lower reaction temperature has been preserved.

The acid sample, following removal of neutral material on DEAE-Sephadex, was dissolved in 25 ml of anhydrous methanol. After the addition of 1 ml (7.5-8.5N) methanolic HCl, the flask was stoppered and the mixture was allowed to react 30-45 min at room temperature. Approximately 90-95% of the excess HCl was neutralized with 1.5N methanolic KOH. The excess methanol was evaporated under vacuum, and the acids were redissolved in 89:10:1 ether-methanol-water and placed on a column of DEAE-Sephadex to fractionate the fatty acid esters and free resin acids. The

slight excess of hydrochloric acid did not affect the DEAE-Sephadex or hinder the separation, but remained at the top of the column. The potassium chloride formed by neutralization was insoluble and was not transferred to the column.

MARGARIC ACID ($C_{16}H_{33}CO_2H$), AN INTERNAL STANDARD

Using the general method of Balder and Crowell (20), margaric acid was used as an internal standard for both resin and fatty acids, and was added prior to the separation of neutral and acidic material on DEAE-Sephadex. The acids were methylated with diazomethane and the esters were purified on a column (1 cm x 4 cm) of Woelm neutral alumina activity III (6% H_2O).

If fatty and resin acids were combined, a differential methylation and fractionation on DEAE-Sephadex was performed prior to addition of the C_{17}-acid. The methyl ester of the C_{17}-acid was added to the fatty acid esters before purification on alumina, and the free acid to the resin acids before methylation and purification.

If the ratio of fatty to resin acids was known initially, the C_{17}-acid could be added before DEAE-Sephadex. Also, due to apparent losses shown by GC analysis, if the neutrals were not removed prior to GC analysis the loss shown with respect to C_{17} would be the sum of the neutrals + actual loss. Therefore, the % neutrals could not be determined accurately.

ATTEMPTED PURIFICATION OF RESIN ACIDS FROM TALL OIL ROSIN

An amount of 21.6 g of Westvaco Rosin R (Westvaco, Charleston, South Carolina) was dissolved in 75 ml of 2N sodium hydroxide and diluted with 175 ml of water by heating the mixture to 90-95°C. To the clear yellow solution was added slowly 100 ml of 2N sodium hydroxide. A copious white precipitate formed and

the mixture was cooled to room temperature under manual stirring. After standing overnight in the refrigerator, the granular precipitate was removed by filtration and was washed with a small amount of 1N sodium hydroxide and the wet sodium resinate was dissolved in water to form 304 ml of solution. The mother liquor filtrate from the sodium resinate, 238 ml, and the washings, 130 ml, were collected separately. The fractions were analyzed by the usual procedures and the results are listed in Table XVI.

SUMMARY AND CONCLUSIONS

1. Oxygen/sodium hydroxide pulping of chips of aspen and slash pine, normal and resin-soaked (Paraquat-treated tree), at a 3.85 liquor/wood ratio, resulted in no practical losses of extractable tall oil components. With liquor/wood ratios of 10, 30-60% losses occurred.

2. When tall oil acids were cooked in oxygen/sodium hydroxide with varied amounts of extractive-free wood, (a) general oxidative destruction of the extractable tall oil and (b) selective oxidations were evident. Among the fatty acids, linoleic was oxidized more rapidly than oleic which was less resistant to attack than the saturated acids, palmitic and stearic. Among the resin acids, abietic acid was oxidized to dehydroabietic acid.

3. The presence of relatively small amounts of wood resulted in a considerable increase in the survival of extractable tall oil. This was interpreted as a consequence of competing reactions among the wood components with lignin as possibly the most reactive. However, carbohydrates were also severely oxidized when pulp yields were 5-6% with concomitant yields of crude tall oil, 40-60%.

4. As compared with chips, the use of fiberized wood, with or without an alkaline pretreatment, resulted in no significant influence on the amount or character of extractable crude tall oil in oxygen/alkali pulping.

5. The small amounts of extractable tall oil which were retained in the washed pulps exhibited somewhat more severe oxidation than that in the corresponding black liquors, but no definitive data were sought on this point.

6. When tall oil acids were cooked in oxygen/sodium hydroxide with fiberized red maple, the formation of dehydroabietic acid from abietic acid was greatly diminished in comparison with the results using loblolly pine. The "protective" action of a hardwood may exceed that of a softwood due possibly to a higher rate of reaction toward the oxygen/sodium hydroxide.

7. When tall oil acids were cooked with extractive-free wood in oxygen/sodium carbonate and /bicarbonate, the losses of extractable tall oil were similar to or greater than the losses in oxygen/sodium hydroxide, with the bicarbonate system somewhat more severe than the carbonate system. With respect to the extractable tall oils the most obvious difference between the cooks with hydroxide and the carbonates was the absence of abietic acid and the prominence of dehydroabietic acid in oxygen/carbonates.

8. The main turpentine components, alpha- and beta-pinene, survived the oxygen/sodium hydroxide cooks in yields of 19-38%. In the carbonates with oxygen the yields were 8-13%. These results indicated the possibility that oxidation mechanisms may differ between hydroxide and carbonate systems when oxygen is present.

9. α-Pinene was oxidized only slightly more rapidly than β-pinene. Small amounts of several unidentified, high-boiling substances appeared in chromatograms of turpentines from the oxidizing cooks.

10. Yields of 10-40% of available turpentine were recoverable in oxygen/alkali pulping. These low yields may preclude the possibility of practical turpentine production in one-stage oxygen/alkali pulping.

SUGGESTIONS FOR FUTURE WORK

Based on the results of work on this project, the evaluation of the levels of dissolved oxygen in the cooking liquor, at temperature, may be important. The proper engineering of digestors both to control pulp yield and pulp quality, and in by-product recovery may depend upon such knowledge. Such data have been obtained on Project 3265 in the study of the action of oxygen/alkali on carbohydrates.

Oxygen/carbonate systems were somewhat more severe in the attack on tall oil and turpentine components than was oxygen/sodium hydroxide. This observation appears to be consistent with a hypothesis of N. S. Thompson, Project 3265, that oxidative species and mechanisms may be different in oxygen/carbonates and bicarbonates. Systematic study of oxygen/alkali reactions in the oxidation of tall oil and turpentine may be helpful. Work of this nature is in progress as a doctoral thesis program by Gerald K. Mittet.

ACKNOWLEDGMENTS

We gratefully acknowledge the work of staff members Mrs. Bruce Alward, Mr. Joel Bichler, and Mr. John Peckham without whose assistance this work could not have been done.

LITERATURE CITED

1. Project 3266, Report One, Dec. 31, 1975.

2. Project 3267, Final Report, Aug. 9, 1976.

3. "Paraquat" is a trade name (Chevron Chemical Co.) for 1,1'-dimethyl-4,4'-bipyridinium dichloride.

4. DEAE-Sephadex, A-25, is a diethylaminoethyl cross-linked dextran, and was obtained from Pharmacia Fine Chemicals, Inc., 800 Centennial Ave., Piscataway, New Jersey 08854.

5. Mutton, D. B. Wood resins. In Hillis' Wood extractives and their significance to the pulp and paper industries. p. 331-61. New York, Academic Press, 1962.

6. Buchanan, M. A., Sinnett, R. V., and Jappe, J. A., Tappi 42:578(1959).

7. Cunningham, A., Martin, S. S., and Langenheim, J. H., Phytochem. 12(3):633-5 (1973).

8. Ref. (1), Table I, p. 6; Table IV, p. 12.

9. Renard, J. J., Mackie, D. M., Jones, H. G., Bolker, H. I., and Clayton, D. W., CPPA Trans. Tech. Sect. 1(1):1-11(March, 1975).

10. Renard, J. J., Mackie, D. M., Bolker, H. I., and Clayton, D. W., Cellulose Chem. Technol. 9(4):341-52(1975); Grangaard, D. H., and Saunders, G. H., U.S. pat. 2,926,114(1960); Can. pat. 611,503(1960).

11. Nicholls, G. A., Jamieson, R. G., and Van Drunen, V. J., Tappi 58(5):105-9 (1975); 59(3):81-4(1976).

12. Marton, R., Brown, A., and Granzow, S., Tappi 58(2):64-7(1975).

13. Mittet, G. R. Degradation of fatty acids, fats and waxes by molecular oxygen in alkaline media. Doctoral Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, in progress.

14. Thompson, N. S., Project 3265, private communication.

15. Saltsman, W., and Kuiken, K. A., Tappi 42:873-4(1959).

16. Zinkel, D. F., Tappi 58:109-11(1975).

17. Laundrie, J. F., and Zinkel, D. F. Yield and quality of kraft pulp and naval stores by-products from artificially lightered slash pine. In Stone's Proceedings, Lightwood Coordinating Council, March, 1975. p. 110.

18. Drew, J., U.S. pat. 3,871,951(March 18, 1975).

19. Drew, J., and Pylant, G. D., Tappi 49(10):430(1966); Pearl, I. A. Chemical utilization of southern pine barks. Project 2753, Report Two, May 23, 1969.

20. Balder, E. E., and Crowell, E. P., J. Am. Chem. Soc. 52:14(1975).

THE INSTITUTE OF PAPER CHEMISTRY

Irwin A. Pearl
Group Leader

Edgar E. Dickey
Senior Research Associate

John W. Swanson
Director
Divison of Natural
Materials & Systems

APPENDIX I

ABSTRACT FROM REPORT ONE

In laboratory scale equipment, loblolly pinewood chips were pretreated with soda (sodium hydroxide) which involved impregnation under pressure followed by steaming. In other experiments chips were pulped by the kraft, soda, and alkali-oxygen (soda-oxygen) processes. More skimmable tall oil soap was obtained from a kraft cook than from soda or alkali-oxygen cooks. However, due to the solubility of the tall oil components in the kraft black liquor, approximately one-third of the tall oil could not be recovered as skimmable soap.

The extractable crude tall oil obtained from the pretreatment liquors was 55-65% of that obtainable from the kraft cooks with a higher yield recovered when a higher concentration of sodium hydroxide was used in the impregnation liquor. Presumably, the balance of tall oil remained in the pretreated fiberized chips. When alkali-pretreated chips were pulped by the kraft process, tall oil was recovered in an amount which, together with that from the pretreatment step, accounted for most of the tall oil potentially available.

The addition of oxygen to a soda cook caused relatively little more loss in tall oil components over that of the soda cook alone. The main change in tall oil components was the marked increase in dehydroabietic acid at the expense of abietic acid. Although the unsaturated fatty acids, oleic, linoleic, and palmitoleic, might be expected to oxidize to other compounds under soda-oxygen conditions, this did not occur, suggesting that these compounds may be as stable in oxygen-alkali pulping as are other tall oil components.

Slash pinewood chips from a normal tree and lightwood (resin-soaked) chips from a Paraquat-treated tree, were pulped by the alkali-oxygen process to

exaggerate possible changes in the tall oil components. The analytical procedures were designed to recover all extractable tall oil as well as to measure skimmable soaps. Aspen was included to afford a comparison with a hardwood in which resin acids were absent. Aspen and the lightwood produced no skimmable tall oil soap. In all cases except the lightwood, the largest fraction of extractable tall oil was recovered from relatively dilute liquors which were obtained in fiberizing the chips in a Waring Blendor. Also, substantial amounts of extractable tall oil were recovered from the pulps upon acidification with dilute sulfuric acid and extraction with acetone. The total extractable tall oil in soda-oxygen pulping suggested that no significant losses of tall oil components occurred as a result of the pulping process.

APPENDIX II

SUMMARY FROM REPORT ONE

1. Even under the optimum conditions of the long cook kraft, approximately one-third of the tall oil components cannot be recovered.

2. Using the long cook kraft yield as the maximum possible commercial tall oil yield, less than 40% of this amount of crude tall oil could be recovered from the soda cook, suggesting that a first-stage soda cook would be unsatisfactory for the commercial production of tall oil.

3. The addition of oxygen to the soda cook caused relatively little more loss in the amount of crude tall oil recovered over that of the soda cook alone. This conclusion must be qualified by the fact that the pulp yield in the soda cook was 79%, while in the soda-oxygen cook, it was 54%.

4. The oxidation by oxygen-alkali of the extractives of loblolly pinewood appears to be a minor factor in the available tall oil.

5. Although the unsaturated fatty acids, oleic acid, linoleic acid, and palmitoleic acid might be expected to oxidize to other compounds under alkali-oxygen conditions, this did not occur, suggesting that these unsaturated acids are stable under conditions of oxygen-alkali pulping to the same extent that other tall oil components are.

6. All of the resin acids were relatively stable to oxygen-alkali pulping conditions except abietic acid which was converted almost entirely into dehydroabietic acid, a major component of tall oil under all conditions.

7. The total crude tall oil yields obtained from the pretreatment (alkaline) liquors amounted to 55-65% of that obtained from the long cook kraft pulping experiment with the higher yield coming from the experiment with a higher concentration of sodium hydroxide in the impregnation liquor. Presumably, the balance of the tall oil remained in the pretreated fiberized chips.

8. When alkali-pretreated chips were pulped by the kraft process, tall oil was recovered in an amount which, together with that from the pretreatment step, accounted for most of the tall oil potentially available.

9. In an attempt to exaggerate the possible effects of the alkali-oxygen process on tall oil components, slash pine lightwood (34% extractives in the resin-soaked wood from a Paraquat-treated tree) was cooked. No skimmable soap was produced. This may be due to the very small proportion of fatty acids relative to resin acids in the extractives.

10. Aspen chips were included in the series to test the survival of hardwood fatty acids (no resin acids were present) in the alkali-oxygen process. No precipitate of soap was formed.

11. In an effort to account for all the extractable tall oil, the analytical procedure was revised to include tall oil present in cooking and washing liquors and adsorbed or occluded on the final pulp. When the procedure was applied to normal aspen and slash pine, the total extractable tall oil indicated that only minor losses of potential tall oil (based on saponified extractives) had occurred. Thus, losses through the action of alkali-oxygen may be less than were indicated originally. The recovery of tall oil from the Paraquat-treated samples was less efficient than from normal wood. With the exception of

the lightwood sample, the largest fraction of the extractable tall oil was recovered from the fiberized chip washings. This may be due, in part, to a slow or repressed diffusion of the tall oil soap from the chips into the cooking liquor. In the kraft process diffusion may be more efficient than in the alkali-oxygen system.

APPENDIX III

ANALYSIS OF REFINED TALL OIL ACIDS

TABLE XVII

ANALYSIS OF REFINED "UNITOLS"[a] ON DEAE-SEPHADEX AND BY DIFFERENTIAL METHYLATION

	Relative Composition, % as received			
	Unitol FA		Unitol RA	
	Given by Mfr.	Found	Given by Mfr.	Found
Neutrals	1.6	1.2	5.2	5.4
Fatty acids	97.4	97.8	3.0	1.8
Resin acids	1.0	<1	91.8	92.8

[a]"Unitol" fatty acids (FA) and "Unitol" rosin (RA), Union Camp, Jacksonville, Florida.

TABLE XVIII

COMPOSITION OF "UNITOL" FATTY ACIDS BY GAS CHROMATOGRAPHY

Chromatographed as Methyl Esters

	Retention Time, min	Unitol Fatty Acids		Stock Solution, FA in NaOH	Fatty Acids Cooked Without Wood	
		Unsapfd. Removed	Unsapfd. Present		In N_2-Alk.	In O_2-Alk.
Fatty Acids, relative cpn., % of FA fraction						
C_{16} Palmitoleic C_{17}		<1	<1	<1	<1	3.7
Stearic	7.9	2.4	2.8	2.7	2.8	7.4
Oleic	9.4	51.0	53.1	54.0	54.2	83.2
C_{19}	10.6	<1	<1	<1	<1	<1
Linoleic	12.0	38.5	38.4	38.2	28.2	5.7
C_{20}	13.6	2.7	1.8	2.0	1.3	--
Linolenic	16.4	2.7	2.3	1.8	10.1	--
Unknown	19.3	2.1	1.6	1.2	2.6	--

TABLE XIX

COMPOSITION OF "UNITOL" RESIN ACIDS BY GAS CHROMATOGRAPHY

Chromatographed as Methyl Esters

Resin Acids, relative cpn., % of RA fraction	Retention Time, min	Unitol Resin Acids		Unitol RA Sapfd.	Resin Acids Cooked Without Wood	
		Unsapfd. Removed	Unsapfd. Present		In NaOH	In O_2-NaOH
Unknown	10.4	<1	<1	<1	<1	3.3
Tetrahydroabietic	12.9	3.0	2.6	3.5	4.0	3.9
Pimaric	14.5	3.0	3.0	4.1	3.2	4.8
Sandaracopimaric	16.4	3.2	2.8	4.5	3.3	3.2
Unknown	18.1	<1	<1	1.6	<1	5.5
Palustric/levopimaric	20.0	8.7	8.7	8.9	7.5	--
Isopimaric	21.2	6.2	6.0	6.6	6.5	8.6
Unknown	23.3	4.0	3.9	4.8	3.5	<1
Unknown	25.8	1.0	1.7	1.6	1.3	--
Abietic	30.9	44.9	43.7	39.2	41.7	<1
Dehydroabietic	34.1	22.6	23.3	21.9	25.1	64.6
Neoabietic	36.2	1.7	1.6	2.2	1.1	--
Unknown	40.7	<1	<1	<1	<1	4.6